Vibrational spectroscopy of intercalated kaolinites. Part I.

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Abstract

The industrial application of kaolinite is closely related to its reactivity and surface properties. The reactivity of kaolinite can be tested by intercalation, i.e. via the insertion of low molecular weight organic compounds between the kaolinite layers resulting in the formation of a nano-layered organo-complex. Although intercalation of kaolinite is an old and ongoing research topic, there is a limited knowledge available on the reactivity of different kaolinites, the mechanism of complex formation as well as on the structure of the complexes formed.

Grafting and incorporation of exfoliated kaolinite in polymer matrices and other potential applications can open new horizons in the study of kaolinite intercalation. This paper attempts to summarize (without completion) the most recent achievements in the study of kaolinite organo-complexes obtained with the most common intercalating compounds like urea, potassium acetate, dimethyl sulphoxide, formamide and hydrazine using vibrational spectroscopy combined with X-ray powder diffraction and thermal analysis.

Introduction

Kaolinite, an important industrial raw material - used extensively as additive and filler in the paper, plastics, rubber, pharmaceutical and polymer industry - is the most abundant mineral of the kaolinite group (also including dickite, nacrite and halloysite) with the chemical formula $Al_2Si_2O_5(OH)_4$. It is a 1:1 phyllosilicate consisting of double layers joined together through apical oxygen atoms. One side of the double layer is gibbsite-like with aluminum atoms octahedrally coordinated with four oxygen atoms and two hydroxyl groups. The other side is a two-dimensional silicate layer structure where silicon atoms are tetrahedrally coordinated with four oxygen atoms. The double layers are joined as sheets to other double layers via hydrogen bonds between the siloxane macrorings and the aluminol surface forming a large set of layers (known as kaolinite book).

Figure 1

Kaolinite can interact with organic molecules by intercalation. In this process the reactive guest molecules enter the interlamellar space, break up the hydrogen bonds and form new ones resulting in a nano-layered material. The basic principles of kaolinite intercalation were reported by Lagaly (1) in 1984. The reactive molecules were classified by Weiss *et al.*

(2) as follows: 1) compounds forming strong hydrogen bonds to the silicate layers, e.g. urea, formamide and hydrazine; 2) compounds with pronounced betain-like character with the possibility of strong dipole interactions with the silicate layer, e.g. dimethyl sulphoxide; and 3) alkali salts of short chain fatty acids, e.g. acetic acid. Non-reactive guest molecules can entrain between the layers by reactive guest molecules. Reactive molecules (e.g. dimethyl sulphoxide, hydrazine) can also be used as precursors for the intercalation of non-reactive organic molecules via the displacement of intercalated molecules. In addition to the formation of new organo-clay nanohybride materials, intercalation can lead to the covalent grafting of organic molecules (3). Kaolinite has the potential to be a precursor for polymer-kaolinite intercalation composites (4).

Vibrational spectroscopy is a key technique in the study of the formation and structural characterization of kaolinite intercalates. Farmer (5) has reviewed the vibrational modes of kaolinite of which the stretching, deformation and translation modes of the OH groups are of utmost importance for structure analysis. The inner surface hydroxyls are connected to the octahedral layers and form hydrogen bonds with the oxygen sheet of the adjacent siloxane layers (Figure 2). The inner OH groups are located in the plane common to the octahedral and tetrahedral sheets and point towards an empty octahedral site. The outer OH groups are at the surface and at broken edges of the crystal.

Figure 2

In the Raman spectrum of kaolinite (Figure 3) five distinct bands can be observed at 3693 (ν_1), 3685 (ν_4), 3670 (ν_2), 3652 (ν_3) and 3620 (ν_5) cm^{-1}. The ν_1-ν_4 bands are assigned to the OH stretching mode of the three inner surface hydroxyl groups. The band at 3620 cm^{-1} is assigned to the stretching mode of the inner hydroxyl group. The band at 3685 cm^{-1} is Raman-

active, infrared-inactive and is observed as a component of an unresolved doublet at 3693/3685 cm^{-1}. The band at 3685 cm^{-1} is ascribed to the transverse optic mode, while the band at 3693 cm^{-1} is assigned to the longitudinal optic mode. This band is of low intensity in the Raman spectrum, but is strongly infrared active. The 3670 and 3652cm^{-1} bands (ν_2 and ν_3) are weak and are described as the out-of-phase vibrational modes of the in-phase vibration observed at 3693 cm^{-1}. The 3620 cm^{-1} inner OH band (ν_5) is strong and sharp. The intensity of the OH stretching bands depends on the structural order of the kaolinite. In less ordered kaolinites the intensity of the ν_1 band is reduced and the 3670 and 3652 cm^{-1} bands cannot always be resolved. In addition to the OH stretching region, the most informative spectral ranges are those of the apical Si-O (1115 cm^{-1}), the Si-O-Si in-plane (1033 and 1008 cm^{-1}), the OH bending (937 and 914 cm^{-1}) and the OH translational (795 and 755 cm^{-1}) vibrations.

Figure 3

Intercalation of urea into kaolinite

One of the earliest infrared studies on urea-intercalated kaolinites was made by Ledoux and White (6) on a Georgia kaolin prepared by washing a hydrazine-kaolinite suspension with saturated urea solution. The IR spectrum of the complex heated at 110 °C for 15 min and recorded on an Irtran window showed „striking reduction" in intensity of the 3695, 3670 and 3650 cm^{-1} bands, the greater resolution of the urea bands in the 1800 – 1500 cm^{-1} range, and the appearance of two additional νNH bands at 3520 and 3415 cm^{-1}. The proposed configuration of the intercalated urea in the clay structure expanded to 10.77 Å was that one NH_2 group is located near the oxygen plane of the tetrahedral sheet and the remaining NH_2 and CO groups are opposite to the inner surface hydroxyls. The potential formation of

hydrogen bonds between the CO group and the inner surface hydroxyls was highlighted with the necessary shift of the νCO band to higher frequencies.

Frost *et al.* (7-9) reported a detailed study on the urea intercalate of a highly ordered kaolinite (Királyhegy, Hungary) with a Hinckley index of 1.39. The remarkable intensity decrease of the outer OH bands and the appearance of additional ones at 3391, 3408 and 3500 cm^{-1} indicated that urea disrupted the interlayer hydrogen bonding between the kaolinite layers. The bands at 3391 and 3408 cm^{-1} are due to the symmetric and antisymmetric vibrational modes of the urea NH groups interacting with the siloxane surface. The stretching vibration of the C=O group at 1679 cm^{-1} was not observed in the intercalate spectrum. The shift of the two Al-OH deformation bands of 916 and 936 cm^{-1} to 905 and 914 cm^{-1} was not interpreted as a possible evidence of hydrogen bonding between the urea C=O and the inner surface OH groups. At liquid nitrogen temperature (77K) no intensity remained in the inner surface hydroxyl stretching bands suggesting that these hydroxyls are hydrogen bonded (through the C=O group) to the inserting molecule. The antisymmetric and symmetric stretching bands appeared at 3421 and 3382 cm^{-1}. Thus, it was concluded that on cooling to 77 K, the urea and hydroxyl groups are brought closer so that hydrogen bonding between hydroxyls of the gibbsite-like layer and the C=O group can occur (10).

Gardolinski *et al.* (11) reported the complete intercalation of an ordered kaolinite (KGa-1b) upon grinding with 20% urea. After washing with water under ultrasound stirring at 363 K and air-drying, a 8.4 Å hydrated kaolinite was obtained. New bands at 3600 and 3556 cm^{-1} indicated different types of water molecules in the hydrated structure.

Yan *et al.* (12) reported a rapid preparation of kaolinite-urea complex (containing 20% urea and 10% water) in a high-speed mixer at 95 °C. FTIR spectroscopy revealed the significant reduction of the 3695, 3668 and 3653 cm^{-1} bands as proof of the incorporation of urea.

Fukumachi *et al.* (13) monitored the thermal decomposition of an Fe^{3+} -containing Brasilian kaolinite mechanochemically intercalated with urea using FTIR spectroscopy. They suggested that urea is connected to the kaolinite layers via hydrogen bonds at two points: through the NH_2 groups connected to tetrahedral oxygens and through the hydroxyl groups of the Fe^{3+}-ions (located in the coordination sphere) connected to the carbonyl groups of urea. The validity of the model was supported by EPR measurements, as well.

Kaolinite from Zettlitz (Sedlec) was intercalated with urea using a combined treatment including dry milling and heat treatment by Walásková *et al.* (14). The positions of the OH bands did not change as a result of intercalation (3698, 3670, 3652 and 937 cm^{-1}) and the new bands were interpreted according to Ledaux and White (6). However, the C=O stretching vibration of urea was observed in the complex at 1683 cm^{-1}. The FTIR spectra of the intercalates washed using ultrasound and thermal procedures showed bands at 3548 and 1654 cm^{-1} corresponding to OH stretching of residual water molecules causing an increase of the interlayer space.

Rutkai *et al.* (15) carried out computer simulations with respect to the possible orientation of urea in the kaolinite-urea complex. It was pointed out that the dipole moment vectors of urea molecules tend to point towards the silica sheet and the character of the hydrogen bonds can be described more precisely by simulation.

A new mechanism of bonding urea to the siloxane surface was proposed by Makó *et al.* (16) based on an FTIR(DRIFT) spectroscopic study. The blue shift of the amide I band at 1673 cm^{-1} in the kaolinite (from Szeg, Hungary) to 1683 cm^{-1} was due to the free C=O vibration since the conjugation between the C=O and NH groups lo longer exists. As a result, hydrogen bonding is formed between the NH group and the siloxane surface. The red shift of the NH_2 deformation band from 1628 to 1615 cm^{-1} is an indication of hydrogen bond formation at the other end of the urea molecule. Another means of following the changes of

the hydroxyl surface is the study of the OH deformation region between 840 and 960 cm^{-1}. After intercalation, the Al-OH deformation band at 916 cm^{-1} shifted to 912 cm^{-1} and a shoulder band appeared at 902 cm^{-1}. The most likely explanation of the 902 cm^{-1} band is that urea delaminates the kaolinite and forces the inner surface hydroxyls to hydrogen bond to the C=O group of urea.

Acetate intercalation into kaolinite

Although kaolinite can easily be intercalated with potassium acetate, a complete reaction cannot be achieved. The reason for this is not known with certainty. E.g. Orzechowski *et al.* (17) studying the dielectric behaviour of intercalated kaolinites came to the conclusion that molecules possessing both proton-donor and proton-acceptor groups could easily be intercalated. The acetate ion has only proton-acceptor capability and can form hydrogen bonds with the gibbsitic sheet, only.

As early as in 1966 Ledoux and White (6) discussed the IR spectrum of a Georgia kaolin intercalated with potassium acetate. They noticed the decrease in intensity of the 3695 cm^{-1} band in the poorly expanded kaolinite and the appearance of a new band at 3600 cm^{-1}. They concluded that the new band may result from the formation of a weak hydrogen bond between the inner surface hydroxyls and the acetate ion. The 1560 and 1420 cm^{-1} bands were due to the antisymmetric and symmetric ν(COO) stretching vibrations. In addition, the presence of the potassium acetate molecules in interlayer positions were interpreted with the X-ray diffraction peak at 11.6 Å, referring to the work of Wada (18) in 1961.

Kristóf *et al.* (19) and Gábor *et al.* (20) studied the behaviour of Hungarian kaolinites intercalated with an efficiency of over 90% with potassium acetate using FTIR spectroscopy, X-ray diffraction and thermal analysis techniques. Dehydration of the complex expanded to

14.1 Å was complete by 200 °C and the melting of the adsorbed acetate took place at 292 °C. The complex was stable up to about 300 °C. Above this temperature dehydroxylation and the decomposition of the acetate to carbonate took place simultaneously. A correlation was found between the relative intensity of the hydrogen-bonded OH stretching band at 3605 cm^{-1} and the decrease in dehydroxylation temperature. It means that the dehydroxylation behaviour of different kaolinites can be predicted from the IR spectrum. In addition, the split of the hydrogen-bonded OH band indicates multi-step dehydroxylation. X-ray diffraction showed the appearance of new peaks at 8.5 Å and 11.5 Å upon heating. Upon exposure to air, the complex re-expanded to the original *d*-value of 14.1Å. This phenomenon was explained by rehydration of the complex

Frost *et al.* (21, 22) used FT-Raman spectroscopy for the structure elucidation of the highly ordered Királyhegy kaolinite intercalated with an efficiency of 95% with potassium acetate. In spite of the incomplete reaction, the total normalized intensity of the ν_1(3695 cm^{-1}), ν_4(3686 cm^{-1}), ν_2(3670 cm^{-1}) and ν_3(3645 cm^{-1}) inner surface OH bands was reduced to 18% as a result of hydrogen bonding with the acetate ion. The fact that only one hydrogen-bonded OH stretching band was observed at 3605 cm^{-1} shows that only one OH-environment is present in the complex. The band area of the inner OH group remained unchanged, but a significant broadening (the half-width changed from 2.9 cm^{-1} to 6.2 cm^{-1}) was observed. The symmetric stretching band of the O-C-O unit at 1420 cm^{-1} in potassium acetate shifted to 1412 cm^{-1} as a result of hydrogen-bonding with inner surface OH groups in the complex. At the same time, the symmetric deformation band of the CH_3 group was reduced in intensity and split into two overlapping bands at 1355 and 1345 cm^{-1}. This means the loss of symmetry of the CH_3 bending vibration. It was proposed that the CH_3 group of the acetate is interacting with the silica sheet. Thus, the final conclusion was made that the acetate ion is anchored at two points (connected to both planes). The Al-OH deformation band at 926 cm^{-1} showed a 10-

fold increase in intensity and is highly polarized with a depolarization ratio of 0.45. These observations indicate that the inner surface OH groups are at an angle approaching 90° to the (001) face in the intercalate.

The acetate can easily be deintercalated from the complex by washing with water (22). After 1 min of washing the degree of intercalation was reduced to 25%, although traces of the expanded complex could be observed even after 1 day. The deintercalation kinetics could be followed by both X-ray diffraction and Raman microscopy.

A systematic study on the spectral changes of the hydroxyl stretching region upon dehydration and rehydration of the kaolinite – potassium acetate complex was made by Frost *et al.* (23, 24). The kinetics of rehydration was studied by X-ray diffraction. Upon heating the complex to 200 °C and cooled back to room temperature in nitrogen atmosphere, two diffraction peaks appeared at 11.68 and 9.72 Å, while the 14.1 Å reflection was missing. Upon exposure to air for 1 min phases were observed with *d*(001) spacings of 14.13, 11.56, 9.88, 8.90 and 8.55 Å. The 14.13 Å phase corresponds to the fully expanded kaolinite, while the 11.56 and 9.88 Å phases correspond to the two expanded phases of the 200 °C pattern. The two expanded phases at 8.90 and 8.55 Å may correspond to the formation of a hydrated kaolinite. After some 20 min the expanded structure has returned to its original *d*-spacing showing the reversibility of the process. When the complex is heated to 50 °C, the 3606 cm^{-1} Raman band is resolved into two bands at 3605 and 3594 cm^{-1}. At 100 °C Raman bands are observed at 3600, 3613 and 3632 cm^{-1}. The band at 3632 cm^{-1} is attributed to the inner OHs. At 150°C the three bands are present at 3600, 3611 and 3633 cm^{-1}. Based on the results of X-ray diffraction and Raman microscopic investigations, a new model was proposed for the location of the acetate ion in the interlayer space. The 14 Å phase with the 3605 cm^{-1} Raman band of the hydrogen-bonded inner surface OH groups corresponds to a vertical orientation of the acetate ion to the (001) plane connected through a water molecule. Upon dehydration the

partial collapse of the complex to 11.6 Å takes place resulting in a stronger bond without water (and a shift of the hydrogen-bonded inner surface OH stretching band to 3595 cm^{-1}). The reflection in the 8.9-9.9 Å range may correspond to the parallel orientation of the acetate ion with the (001) plane. The corresponding Raman band at around 3611 cm^{-1} therefore represents a weaker hydrogen-bond.

Cruz *et al.* (25) also reported the appearance of the two new reflections at 11.7 Å and 9.4 Å upon heating a Cornwall kaolinite expanded with potassium acetate. In their interpretation these reflections correspond to complexes with two different interlayer structures. They believed that water is still present even in the "dehydrated" complex suggesting the formation of hydrogen bonds between the inner surface of kaolinite and water.

Frost *et al.* (26-29) intercalated potassium acetate into kaolinite under high pressure and temperature. Intercalation under 20 bars pressure at 220°C caused the differentiation of the hydrogen-bonded inner surface OH bands. In the Raman spectrum these bands were found at 3590, 3603 and 3609 cm^{-1}, while the DRIFT spectrum showed new bands at 3995 and 3605 cm^{-1}. Additional bands were also found in the OH deformation range at 895 and 906 cm^{-1}. It was concluded that the high pressure and temperature result in the differentiation of the inner surface hydroxyl groups and the decrease in structural order as well, leading to the formation of more defect structures. Upon cooling to liquid nitrogen temperature, the separation between the stretching bands of the inner hydroxyl and the inner surface hydroxyl groups hydrogen-bonded to the acetate decreases (the opposite tendency was expected). The first band shifted from 3620 to 3615 cm^{-1}, while the second shifts from 3605 to 3607 cm^{-1}. This indicates a weaker hydrogen bond formation in the complex at 77 K (30).

Changing the K^+-cation to Cs^+ resulted in a drastic change in the intercalation pattern of kaolinite (31). The intercalation is incomplete, and two hydrogen-bonded inner surface OH bands appear at 3006 and 3595 cm^{-1} in the Raman spectrum. Under hydrothermal conditions

the degree of intercalation is even less, and water is incorporated into the kaolinite structure as indicated by the appearance of a water OH band at 3599 cm^{-1}. In addition, treatment with cesium acetate at 220 °C and 20 bar pressure introduced significant disorder in the kaolinite structure.

The highly hydroscopic nature of the complex makes the infrared study of the OH stretching range difficult. Kristóf *et al.* (32) heated the complex to 130 °C and rehydrated under D_2O to improve the resolution of inner surface and water OH bands. A detailed study by means of thermogravimetry combined with mass spectrometry was also carried out by Kristóf *et al.* (33). Dehydroxylation took place in three overlapping mass loss stages at 334, 376 and 446 °C, simultaneously with the decomposition of intercalated cesium acetate. The water evolution steps at 334 and 376 °C belong to the dehydroxylation of inner surface hydroxyls hydrogen-bonded to acetate ions, while the water formation step at 446 °C represent the dehydroxylation of the non-intercalated fraction. Thus, it can be supposed that in the cesium acetate intercalate two different environments exists for the OH groups accessible by the intercalating acetate ions. This difference can be due to the larger size of the cesium cation which – dissimilarly to the potassium cation – does not fit into the ditrigonal cavity of the tetrahedral layer.

A near-IR spectroscopic study of the potassium and cesium acetate intercalated kaolinites was reported by Frost *et al.* (34). Three spectral regions were identified: the high wavenumber region between 7400 and 6400 cm^{-1} was attributed to the first overtone of the hydroxyl stretching mode, the 5400-4800 cm^{-1} range was attributed to water combination modes, while in the 4800-4000 cm^{-1} region combination bands of the stretching and deformation modes of Al-OH units were reported. This technique has a great potential to distinguish kaolinite and water OH bands that overlap in the mid-IR range, but such an overlap does not occur in the near-IR range.

The effect of mechanochemical activation on the acetate intercalation into kaolinite was studied by Frost *et al.* (35, 36). Since mechanochemical treatment (dry grinding) disturbs the long range ordering in the layers, Raman spectroscopy is not suitable and FTIR (DRIFT) spectroscopy is the technique of choice for the study of changes on the kaolinite inner surface. The relative intensities of both the 3695 and 3620 cm^{-1} bands decreased almost exponentially with the increase of the grinding time. At the same time, the bands in the 3200-3600 cm^{-1} region attributed to the OH stretching vibration of water increased significantly. It was proposed that mechanochemical activation of the kaolinite caused the conversion of the hydroxyl groups to water which coordinated to the kaolinite surface. The amount of intercalation was correlated with the relative intensity of the 3605 cm^{-1} band that also decreased significantly with the time of grinding indicating the loss of layer stacking that prevented intercalation of the kaolinite.

Qu *et al.* (37) came to similar conclusion considering the reaction and orientation of potassium acetate in the kaolinite-potassium acetate complex. They reported the perpendicular position of the acetate between the layers and the shift of the hydrogen-bonded inner surface hydroxyls to lower wavenumbers upon heating.

The intercalation of potassium acetate together with water was also reported by Xia *et al.* (38). They also confirmed the stability of the intercalation complex up to about 400 ºC.

Formamide-intercalated kaolinites

Early works have indicated the reactivity of formamide towards the intercalation of kaolinite due to possessing both donor (NH) and acceptor (C=O) sites (1, 6). Frost *et al*. (39) used Raman microscopy for studying the structure of the Királyhegy kaolinite intercalated in aqueous formamide solutions in the 77 K to 423 K temperature range. On cooling the pure

kaolinite to 77 K, the inner OH band shifts from 3620 cm^{-1} to 3615 cm^{-1}, while the inner surface OH bands shift to higher wavenumbers by 8 - 10 cm^{-1}. In the complex at 298 K the band at 3627 cm^{-1} is attributed to the inner surface OH groups hydrogen-bonded to the C=O unit of formamide. This band shifts to 3631 cm^{-1} at 77 K. The broad band at 3600 cm^{-1} in the 298 K spectrum is observed at 3589 cm^{-1} at 77 K and is attributed to water molecules incorporated into the interlayer space. The band observed at 3463 cm^{-1} at 298 K appears at 3451 cm^{-1} in the 77 K spectrum and is due to the symmetric stretching of the NH group hydrogen-bonded to the siloxane surface. The fact that no intensity left in the inner surface OH range indicates complete expansion of the kaolinite. On heating the complex to 373 K, the 3463 cm^{-1} band of the –N-H···O-Si unit disappears and the deintercalation of the complex is complete by 423 K.

A comparative study of Georgia kaolinites on oriented samples intercalated with ethanolic formamide solutions carried out by Raman and IR microscopy showed the appearance of two hydrogen-bonded inner surface OH bands in ordered clays at 3627 and 3610 cm^{-1} (40). These bands were Raman active and infrared inactive. When these two additional bands were observed in the OH stretching region, then two bands were found for the C=O region, as well. Models for the intercalation of formamide into kaolinites were proposed by the authors.

Wang *et al.* (41) also found two Raman active, infrared inactive bands at 3628 and 3610 cm^{-1}. They concluded that the C=O group is linearly linked with the inner surface OH group and that the vibration is highly symmetric. In the NH stretching region of the DRIFT spectrum two bands corresponding to two types of hydrogen bonds between the formamide NH group and the siloxane layer were found at 3336 and 3466 cm^{-1}. The shift of the Al-OH deformation band from 930 to 933 cm^{-1} was due to the keying of the NH group into the kaolinite ditrigonal cavity.

A comparative study of low and high defect kaolinites (from Királyhegy and Szeg, Hungary) intercalated with formamide and water/formamide mixture by X-ray diffraction, DRIFT, Raman and thermal analysis techniques was made by Frost *et al.* (42, 43). In the presence of water the amount of formamide connected to the kaolinite inner and outer surfaces was 2.38 mol/mol inner surface OH. This figure was 0.77 mol/mol when pure formamide was used for intercalation, only. Only one hydrogen-bonded OH stretching band was observed in the Raman spectrum of the clays studied at 3627 cm^{-1}. In the DRIFT spectra an additional band occurred at 3606 cm^{-1} attributed to non-hydrogen-bonded water involved in the intercalated structure. The presence of the water bending vibration at 1597 cm^{-1} also confirms that water functions as a space-filling molecule in isolated form.

Kristóf *et al.* (44) and Frost *et al.* (45-47) made a systematic study of formamide intercalated low- and high-defect kaolinites using controlled-rate thermal analysis (CRTA). With this technique thermal decomposition reactions can be conducted at a very low and constant rate (e.g. 0.10 mg/min) under conditions close to thermodynamic equilibrium. With this method the adsorbed formamide (present on both the inner and outer surfaces) and the intercalated (hydrogen-bonded) formamide could be completely separated. Independently of the preparation conditions, the non-bonded (i.e. adsorbed) formamide was lost in an isothermal fashion at 118 °C for all kaolinites studied. Knowing the amount of dehydroxylation water liberated from the thermally deintercalated kaolinite between 400 and 600 °C, the amount of formamide connected via hydrogen bonding to the inner surface OH groups was calculated as 0.25 mol/mol inner OH. (It means that complete expansion of the kaolinite to 10.16 Å does not necessarily mean that all inner surface OH groups are in hydrogen bonding).

The effect of mechanochemical activation on the formamide intercalation into a high defect kaolinite has been studied by using X-ray diffraction, thermal analysis and DRIFT

techniques by Frost *et al.* (48). Mechanochemical activation reduced exponentially the intensities of the inner surface OH bands of the kaolinite and simultaneously increased the intensity of water OH bands. The intensity of the NH stretching bands could be used to indicate the degree of intercalation which also decreased with the time of grinding. The position of the amide C=O band was found to be most sensitive to the changes in the local environment (i.e. in the condition of the layer structure).

The formation of superactive centers in thermally treated formamide intercalated kaolinite has been reported by Horváth *et al.* (49). Online TG-MS and offline DRIFT studies showed that after the removal of adsorbed and intercalated formamide on heating, a third type of formamide mass loss stage can be found between 230 and 350 °C due to the *in situ* decomposition for NH_3 and CO. These decomposition products are bonded differently to the superactive surface developed by the combination of grinding, intercalation and thermal deintercalation. The structural variance of the surface species found (e.g. various types of carbonates) was systematically studied as a function of the grinding time, degree of intercalation and thermal treatment by DRIFT spectroscopy.

Intercalation of dimethyl sulphoxide into kaolinite

The vibrational spectroscopic study of dimethyl sulphoxide (DMSO) intercalation has long been in the focus of kaolinite research. As early as in 1984 Johnston *et al.* (50) made a comparative Raman – IR study on a Georgia kaolinite intercalated with a DMSO solution containing 9% water. New bands were reported at 3661, 3538 and 3502 cm^{-1} of which the later two bands appeared in the IR spectrum, only. Based on the intensity decrease of the 940 cm^{-1} Al-OH deformation motion and that of the S=O stretching in the Raman spectrum it was supposed that DMSO forms hydrogen bonds with the inner surface OH groups. New bands in

the CH stretching region also confirmed the highly ordered conformation of the methyl group. Keying of the reagent into the ditrigonal cavity was hypothesized in harmony with Olejnik *et al.* (51) and Thompson *et al.* (52).

Induced disorder by deintercalation of DMSO from well-crystallized kaolinites was studied by Heller-Kallai *et al.* (53) using low temperature IR spectroscopy. It was concluded that the degree and type of disorder depended on the starting material and the method of deintercalation (heating or washing with water).

A new method for DMSO intercalation into kaolinite under hydrothermal conditions was reported by Vempati *et al.* (54). Yields of over 90% could be achieved in 20 min upon heating 1g kaolinite in 10 cm^3 DMSO in a Parr bomb at 150 °C. The FTIR analysis showed the disappearance of the Al-OH deformation band at 941 cm^{-1}. The bands at 3540 and 3505 cm^{-1} were due to the formation of "moderately strong" hydrogen bonding between some of the inner surface hydroxyls and the sulphonyl oxygen.

Frost *et al.* (55) reported the FTIR (DRIFT) and Raman microscopic study of an ordered and a disordered kaolinite (from Királyhegy and Szeg, Hungary) fully expanded with pure DMSO at 85 °C for 7 days in a closed vial. Raman (and IR) bands appeared at 3660, 3536 and 3501 cm^{-1}. An additional band was observed for the low-defect kaolinite only at 3598 cm^{-1} attributed to interlamellar water. The 3660 cm^{-1} band was assigned to the inner surface hydroxyls hydrogen-bonded to the S=O group. The other bands were attributed to the OH stretching frequencies of water in the intercalation complex. The symmetric CH stretching band of DMSO at 2911 cm^{-1} split into two bands at 2917 and 2935 cm^{-1}. It means two different symmetric CH vibrations in the complex. The 2996 cm^{-1} (antisymmetric) CH band split into four bands at 2998, 3015, 3021 and 3029 cm^{-1}. The decrease in degeneracy means four different asymmetric CH stretching vibrations. These observations are in harmony with those of Johnston *et al.* (50). All CH bands showed considerable narrowing upon

intercalation. This supports that the methyl groups are held in a rigid structure. The in-plane methyl deformation vibration band of DMSO at 1419 cm^{-1} was also split into two bands at 1411 and 1430 cm^{-1}. The single intense band at 905 cm^{-1} attributed to the deformation of the inner surface OH groups hydrogen-bonded to the S=O group of DMSO suggests that only one type of hydrogen-bonded inner surface OH group is formed. The water bending vibrations at 1610 and 1683 cm^{-1} indicated two different types of water molecules present. The two S=O stretching bands at 1023 and 1010 cm^{-1} were assigned to two different types of DMSO molecules. In the proposed model two types of DMSO can be distinguished. Type 1 DMSO represents two DMSO molecules linked together via one water molecule. Type 2 DMSO means single DMSO molecules hydrogen-bonded to the kaolinite inner surface OH groups.

The presence of two different types of DMSO complex was confirmed by Kristóf *et al.* (56) with combined thermoanalytical techniques. Upon heating the complex in nitrogen atmosphere, DMSO was liberated in two separate steps at 117 and 173 °C in a ratio of 2:1. The multi-step evolution of DMSO from the kaolinite-DMSO intercalate was also reported by Franco *et al.* (57). In addition, water was also liberated at 77 °C and in a small amount at 177 °C proving the presence of water in the intercalated structure. Upon cooling the complex to 77 K, the hydrogen-bonded inner surface OH stretching band is resolved into two bands at 3658 and 3663 cm^{-1} (58). It was proposed that the DMSO molecule exists with two different orientations in the intercalate differentiated by the two OH stretching bands. In the low-defect kaolinite-DMSO complex four symmetric stretching CH bands can be observed at 77 K at 2937, 2920, 2917 and 2907 cm^{-1}. The antisymmetric band was split into six component bands at 3030, 3023, 3012, 3000, 2994 and 2986 cm^{-1}. Further decrease in degeneracy means that DMSO is locked rigidly into the intercalate structure (59).

The DRIFT and Raman spectroscopic study carried out by Martens *et al*. (60, 61) on the Királyhegy kaolinite intercalated with deuterated DMSO confirmed the presence of two types of intercalated water and DMSO in the intercalate, as well.

FTIR spectroscopy was used to follow the formation of different phases of hydrated kaolinite obtained by washing of a highly ordered Brasilian kaolinite intercalated by DMSO by Gardolinski *et al.* (62).

Since DMSO is a small molecule with high dipole moment, its intercalation into the kaolinite structure can be enhanced with microwave irradiation (63). FTIR spectroscopy was used to follow the process of intercalation. Yields of over 80% could be achieved within 1 min.

FTIR spectroscopy was also used to study the principles of microwave action by Zhang *et al.* (64).

Li *et al.* (65) studied the mechanisms of DMSO intercalation and exfoliation of kaolinite under microwave radiation using FTIR spectroscopy together with X-ray diffraction and thermal analysis.

Although highly sophisticated instrumental methods (e.g. solid state NMR spectroscopy) are used in addition to infrared and Raman spectroscopy to study organoclays, the structure of DMSO in kaolinite is still not known exactly. However, the vibrational spectroscopic results can be used as input data for theoretical calculations of the possible structure (s). The computational models obtained by molecular dynamics simulations (66), geometry optimization (67) and DFT calculations (68) are in good agreement with experimental findings and suppose the keying of one of the methyl groups into the ditrigonal cavity, while the second methyl group is oriented such that the S-C bond is almost parallel with the plane of the inner surface hydroxyl groups.

Hydrazine intercalation into kaolinite

Since hydrazine – in addition to DMSO – is the most reactive reagent towards kaolinite intercalation causing almost complete expansion of the mineral, early attempts were made for the vibrational spectroscopic characterization of the kaolinite-hydrazine complex (6). In addition to the drastic reduction in intensity of the inner surface OH bands and the appearance of new bands in the NH stretching region at 3365 and 3310 cm^{-1}, the partial collapse of the complex from 10.4 Å to 9.4 Å was observed and the presence of occluded water was suspected.

Johnston and Stone (69) first reported Raman spectra for the kaolinite-hydrazine complex and presented lower wavenumber IR and Raman data. In their work on a Georgia kaolinite under reduced pressure described the appearance of an inner surface OH band at 3628 cm^{-1} which had not been observed previously. The partial collapse of the intercalate from 10.4 Å to 9.6 Å was supposed to be due to the keying of the $–NH_2$ moiety upon intercalation of hydrazine into the ditrigonal cavity. The appearance of the 3628 cm^{-1} band was interpreted as the blue-shift of the 3620 cm^{-1} inner OH band as a consequence of this keying effect.

Frost *et al.* (70) supposed that the expansion to 9.48 Å arises from the intercalation of hydrazine alone and the expansion to 10.28 Å is due to the intercalation by hydrazine hydrate. The band at 3628 cm^{-1} was attributed to the OH stretching frequencies of the inner surface hydroxyls hydrogen-bonded to hydrazine. Purging the complex with nitrogen or exposing to air resulted in the loss of intensity of this band. Upon exposure to air, two additional bands appeared with increasing intensity at 3600 and 3555 cm^{-1} and were attributed to water. In the water bending region bands were observed at 1578, 1612, 1627, 1650 and 1679 cm^{-1}. The band at 1578 cm^{-1} was attributed to non-hydrogen-bonded water in the interlayer space. The

1612 cm^{-1} band was accounted for water in the first hydration sphere of hydrazine, while the one at 1627 cm^{-1} was due to adsorbed water. Hydrazine has a band at 1628 cm^{-1} assigned to the H-N-H bending mode. However, if hydrazine is present as a base such as $[NH_2\text{-}NH_3]^{\delta+}OH^-$, this band should not occur in the spectrum. Since bands which occur above 1620 cm^{-1} are normally assigned to strongly coordinated water, the bands at 1650 and 1679 cm^{-1} were attributed to water molecules hydrogen-bonded to hydrazine in the intercalate. Upon exposure to air, the 1650 cm^{-1} band showed a marked increase in intensity, the hydrazine was lost, the *d*-spacing was reduced to 8.8 Å, and the water molecules filled part of the interlayer space. It was suggested that the 8.8 Å intercalated kaolinite was similar to the 8.4 Å synthetic hydrated kaolinite obtained by washing e.g. a DMSO-intercalated kaolinite (71). Isolated water molecules appeared to be keyed into ditrigonal holes of the 8.4 Å hydrate and were referred to as "hole water".

A detailed deintercalation study was carried out on the Királyhegy kaolinite fully intercalated with hydrazine and a new concept for the possible structure of the hydrazine intercalated kaolinite was proposed by Klopprogge *et al*. (72) and Frost *et al*. (73, 74). The DRIFT spectrum showed only one band at 3626 cm^{-1} with a shoulder at 3620 cm^{-1} belonging to the inner OH. No intensity was observed in the ν_1-ν_3 OH stretching range at all. Upon exposure to air, the intensity of the 3626 cm^{-1} band gradually decreased, while the ν_1-ν_3 bands appeared and their intensity increased. At the same time, a new band appeared at 3599 cm^{-1} and increased in intensity. The 3626 cm^{-1} band was attributed to the inner surface OH groups hydrogen-bonded to hydrazine. (In the potassium acetate - intercalated kaolinite the hydrogen-bonded inner surface OH groups produced a peak at 3605 cm^{-1}. Hydrazine can form a weaker hydrogen-bond than the acetate ion, thus it is reasonable to suppose that the hydrogen-bonded inner surface OH band appears at 3626 cm^{-1}).The place of the decomposed hydrazine was replaced by intercalated water as indicated by the 3599 cm^{-1} band. In the

Raman spectrum only the band of the inner OH groups appears at 3620 cm^{-1}. It seems that the inner surface OH groups do not show Raman activity at all in the complex. Upon exposure to air, the complex is decomposed and the original kaolinite spectrum was regained. Both the DRIFT and Raman spectra showed complexity in the NH stretching range with two sets of NH symmetric and antisymmetric stretching bands. Significant changes were also observed in the hydroxyl deformation and water bending modes as a result of deintercalation. Based on the infrared-active, Raman-inactive nature of the inner surface OH bands in the complex, the insertion of a hydrazine-water unit as $[NH_2\text{-}NH_3]^{\delta+}OH^-$ was supposed. In the complex the hydrated end of the hydrazine molecule hydrogen bonds with the inner surface OH groups resulting in the formation of the 3626 cm^{-1} band.

Kristóf *et al.* (56) could prove that water and hydrazine co-exist in the complex. With thermogravimetry combined with mass spectrometry (TG-MS) it was shown that water and hydrazine simultaneously released up to about 100 °C on heating in nitrogen atmosphere. Above 100 °C hydrazine showed another evolution stage without water. This observation is in harmony with the idea of hydrazine hydrate intercalation into kaolinite and that of the existence of hydrazine alone in the complex.

A controlled rate thermal analysis (CRTA) study of the Királyhely kaolinite - potassium acetate complex was carried out by Kristóf *et al.* (75). The complex was heated in a thermobalance in nitrogen atmosphere at a pre-set, constant decomposition rate of 0.15 mg/min. Under these conditions adsorbed and bonded types of hydrazine could be distinguished in the kaolinite. Adsorbed hydrazine was lost in an isothermal step at 46 °C. Type 1 hydrazine (0.20 mol hydrazine hydrate/mol inner surface OH) liberated between 50 and 70 °C in a quasi-isothermal course. Type 2 hydrazine reagent (0.12-0.15 mol hydrazine hydrate/mol inner surface OH) was liberated between 70 and 90 °C. Type 3 reagent (0.30 water-free hydrazine/mol inner OH) was lost in the 85-130 °C range. When the complex was

heated to 70 °C under CRTA conditions, a new reflection appeared at 9.6 Å, in addition to the 10.3 Å one. This new reflection disappeared in contact with moist air and the complex re-expanded to the original d-value of 10.3 Å. As a conclusion, the 9.6 Å reflection was interpreted as the expansion of the kaolinite with hydrazine alone, while the 10.3 Å one was due to expansion with hydrazine hydrate.

The Raman spectrum of the kaolinite – hydrazine complex was investigated by Martens *et al.* (76) at a temperature of 77 K. The inner hydroxyl stretching band in the complex appeared at 3620 cm^{-1} at room temperature. At 77 K this band appeared at 3616 cm^{-1} (similarly to the room temperature pattern, no other bands were observed at 77 K). Then the complex was partially decomposed in moist air. Upon obtaining the Raman spectrum of the partially deintercalated kaolinite at 298 K, two new bands appeared at 3613 and 3622 cm^{-1}, in addition to the normal inner surface hydroxyl bands. Upon obtaining the spectrum at liquid nitrogen temperature, the 3613 cm^{-1} band was observed at 3607 cm^{-1} and the 3622 cm^{-1} band shifted to 3625 cm^{-1}. Thus, the 3625 cm^{-1} band was assigned to the inner surface hydroxyls hydrogen-bonded to hydrazine. The 3613 cm^{-1} band observed at 298 K shifted to 3607 cm^{-1} when cooling to 77 K and was due to water released during the partial deintercalation of the complex. Upon obtaining the Raman spectrum of the hydrazine – intercalated kaolinite heated up to 358 K, the 3627 cm^{-1} band was observed with increasing intensity, but no band was observed at 3607 cm^{-1}. This supports the idea that water was released during de-intercalation. It was supposed that water and/or water –hydrazine together was lost leaving a “pure” hydrazine – intercalated kaolinite behind. The Raman spectrum of the hydrazine – intercalated kaolinite shows two antisymmetric NH stretching bands at 3367 and 3362 cm^{-1}, and two symmetric NH stretching bands at 3301 and 3287 cm^{-1}. This indicates two slightly different NH_2 units in the hydrazine – intercalated kaolinite, one of which is more strongly hydrogen-bonded than the other. One possibility is that one NH_2 unit bonds to the siloxane surface and

the second to the hydroxyl surface. In addition, the possibility of a hydrazine-hydrazine bonding could not be ruled out.

Johnston *et al.* (77) carried out a detailed infrared study of the KGa-1 Georgia kaolinite combined with inelastic neutron scattering and X-ray powder diffraction. Upon wetting the kaolinite with a few drops of anhydrous hydrazine on a ZnSe disk, the expansion to 10.3 Å *d*-spacing was observed in 2 hours with 95% efficiency. Placing the 10.3 Å complex in an IR gas cell under vacuum, the 9.5 Å was produced. The appearance of the 3628 cm^{-1} band was considered as an indication of the partial collapse of the complex (this band did not appear in the fully expanded mineral). The 9.5 Å phase could also be produced by thermal treatment heating the complex to 55 °C (78). The appearance of two new bands at 3465 cm^{-1} and 3568 cm^{-1} in the IR spectrum of the fully expanded mineral was attributed to red-shifted OH stretching bands hydrogen-bonded with hydrazine with a separation of 103 cm^{-1}. The bands at 3695, 3668 and 3652 cm^{-1} reduced significantly in intensity and no measurable perturbance of the inner OH groups was observed. Upon partial collapse of the intercalate to 9.5 Å, the inner OH band was reported to shift to 3628 cm^{-1} with a shoulder at 3620 cm^{-1}. In addition, the 3568 and 3465 cm^{-1} bands disappeared, there was a loss in intensity in the 3650-3670 cm^{-1} region, and a broad band appeared at 3270 cm^{-1}. While the 3628 cm^{-1} band was assigned by Frost *et al.* (73) to hydrogen-bonded inner surface hydroxyl groups supposing that the hydrogen bond with hydrazine cannot be stronger than that with the negatively charged acetate ion, these authors assigned this band to perturbed inner OH groups. The reason for this blue-shift was the supposed partial keying of hydrazine into the siloxane ditrigonal cavity. The narrowing of the bandwidth, the fact that the appearance of this band corresponds directly with the formation of the 9.5 Å complex, and that the gallery height of 2.4 Å is two small to accommodate the hydrazine in the interlamellar region without keying were considered as additional evidence. Based on the study of the NH stretching region, the

existence of hydrogen-bonded and non-hydrogen-bonded NH_2 groups was supposed in both complexes. In addition, intermolecular hydrogen bonding between adjacent hydrazine molecules were also supposed.

Deng *et al.* (79) made an exhausting discussion on the possible molecular configurations and orientations of hydrazine in a study using a Georgia kaolinite. Investigating the effect of water on the intercalation of the kaolinite they observed that intercalation complexes with 10.3 Å and 9.6 Å *d*-spacings were formed using hydrazine monohydrate and anhydrous hydrazine reagents, respectively. When the 9.6 Å complex prepared with anhydrous hydrazine was exposed to air, the complete expansion to 10.3 Å was observed in a hour as a result of water uptake. This observation was in harmony with that of Frost *et al.* (73). Based on a detailed comparison of the IR spectra of the 10.3 Å and the 9.6 Å complexes upon successive heating and exposure to air, they found two possible reasons for the differences in *d*-spacings when anhydrous hydrazine and hydrazine monohydrate was used. One possibility is that water is involved in the intercalation. The other one is that the orientation of hydrazine molecules in the interlayer is changed induced by water molecules. The 9.6 Å complex was explained by the eclipsed form (parallel orientation with the (001) plane) of hydrazine molecules in the complex. With this configuration (four hydrogen atoms face the basal oxygen surface and two nitrogen atoms form hydrogen bonds with their lone pairs with the inner surface OH groups) a higher dipole moment can be obtained which can enhance intercalation. It was stated that this unique interaction might induce the 3626 cm^{-1} OH stretching band observed in the spectrum. The 10.3 Å complex was explained by a configurational change of the hydrazine molecules promoted by water molecules present. In this process the eclipsed form is converted to the common *gauche* form which is stabilized by a more polarized NH_3-NH tautomer structure. For an optimal interaction with the clay surface a tilt of the N-N bond with 30° from the (001) plane is needed, causing the complex to expand

from 9.6 Å to 10.3 Å. This tautomerization, however, is hindered by a high energy barrier, but the mineral can act as a catalyst in this process.

Concluding remarks

The industrial importance of kaolinite-type minerals can justify the increasing interest towards the preparation and application of organoclay nano-composites. Although a great progress has been made since the discovery that the "non-expanding" kaolinite can also be intercalated, further work is need to fully understand the parameters responsible for reactivity, the mechanism of the process of intercalation and the structure of the complexes formed. In this work the application of infrared and Raman spectroscopy is indispensable. However, the complementary use of X-ray diffraction and thermal analysis is also necessary for the characterization of these complicated systems.

Legends

Figure 1. Scanning electron microscopic image of an ordered kaolinite showing kaolinite stacks and book.

Figure 2. Model of the kaolinite unit cell.

Figure 3. Raman spectrum of the kaolinite OH stretching region.

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Concluding remarks

The industrial importance of kaolinite-type minerals can justify the increasing interest towards the preparation and application of organoclay nano-composites. Although a great progress has been made since the discovery that the “non-expanding” kaolinite can also be intercalated, further work is need to fully understand the parameters responsible for reactivity, the mechanism of the process of intercalation and the structure of the complexes formed. In this work the application of infrared and Raman spectroscopy is indispensable. However, the complementary use of X-ray diffraction and thermal analysis is also necessary for the characterization of these complicated systems.

Legends

Figure 1. Scanning electron microscopic image of an ordered kaolinite showing kaolinite stacks and book.

Figure 2. Model of the kaolinite unit cell.

Figure 3. Raman spectrum of the kaolinite OH stretching region.

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